

mula is most likely $C_{16}H_{32}$; and if bromine forms the bibromide, $C_{16}H_{32}Br_2$, from which by the action of caustic soda HBr is abstracted, the compound analyzed would be $C_{16}H_{31}Br$, which formula requires 26·4 per cent. of bromine, whilst the analysis gave 25·8 per cent.; the hydrocarbon would then be an isomer of cetene.

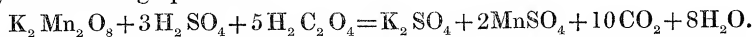
III. "On the Laws of Connexion between the conditions of a chemical Change and its Amount." By A. VERNON HARCOURT and W. ESSON. Communicated by Sir B. C. BRODIE, Bart., F.R.S. Received September 5, 1865.

(Abstract.)

The amount of a chemical change under any conditions which allow of its completion, depends ultimately upon the amount of that one of the substances partaking in it which is present in the smallest proportional quantity. But if the change be arrested before any one of the reagents is exhausted, its amount depends upon the conditions under which it has occurred. These conditions, in the simplest cases, are the quantity of the several reagents, their temperature, and the time during which they have been in contact. The laws of connexion between these conditions of a chemical change and its amount are the subject of an investigation upon which the authors have entered. An account of the first stage of this investigation is contained in the present paper.

Although every chemical change is undoubtedly governed by certain general laws relating to the conditions under which it occurs, the number of cases in which the investigation of these laws is possible is extremely limited. For it is requisite both that the amount of change should be readily estimated, and also that all the conditions affecting it should be susceptible of measurement and of such independent variations as must be made in order to determine the separate influence of each.

The first reaction chosen for investigation was that of permanganic acid upon oxalic acid. It is well known that when a solution of potassic permanganate is added to a solution containing an excess of oxalic acid and sulphuric acid, a change takes place which in its final result is represented by the following equation:—



This reaction occurs at the ordinary temperature; it is thus comparatively easy to keep the temperature of the solution absolutely constant during its progress. It occupies, under a due arrangement of other conditions, a convenient interval of time, and can be started and terminated at a given moment. The reagents are readily obtained in a state of purity, and can be accurately divided and measured as liquids. Lastly, no other condition besides those named affects the result: when each of these is fixed, the amount of change observed in successive experiments is always the same. Nevertheless this reaction, as appeared in the course of its investigation, is

not well adapted to the purpose in view. It is not chemically simple. More than one change occurs under the circumstances of the experiment, and the equation above written represents only a net result. But the examination of a second and simpler reaction in which the authors are at present engaged, has confirmed an explanation which had already suggested itself to them of the results of this series of experiments, and thus they are now enabled to present these results together with a theory which explains and is supported by them.

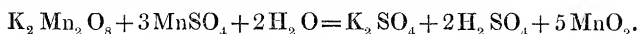
The effect of varying the amount of each of the reagents and the duration of the action was successively investigated. The remaining condition of temperature was not made the subject of experiment, owing to the discovery of the complex nature of the chemical change. A series of Tables contain the numerical results of these experiments. The principal complication arises from a secondary reaction which takes place between permanganic acid and the manganous salt formed by its reduction. It became necessary, in consequence of this action, to include manganous sulphate among the reagents the effect of whose variation was to be determined.

The general method of experimenting was briefly as follows:—Measured quantities of the standard solutions of oxalic acid, sulphuric acid, and manganous sulphate were mixed with a measured quantity of water and the whole brought to a temperature of 16° C. A measured quantity of a standard solution of potassic permanganate was added, and the time of the addition noted. Throughout the course of the action the temperature, observed by means of a thermometer passing into the fluid, was kept rigorously constant. When the required interval had elapsed, an excess of potassic iodide was thrown in, and the liberated iodine, which furnishes an exact measure of the residual permanganic acid or manganic oxide, estimated by means of a standard solution of sodic hyposulphite. The amount of chemical change occurring in any given time with any given amounts of the several reagents can thus be determined.

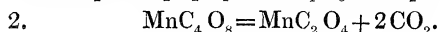
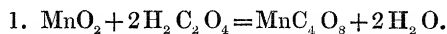
1. *Variation of Sulphuric Acid.*—Each experiment of this series was allowed to proceed for four minutes. Oxalic acid and potassic permanganate were employed in the proportions in which they act one upon another. The quantity of sulphuric acid was varied from the proportional quantity up to seven times that amount. A regular increase in the amount of chemical change within the allotted time occurs with each increment of sulphuric acid. The relation of these quantities, which formed the subject of many series of experiments, is, however, of a complex character. Two or three reactions, it is shown, occur simultaneously, and each of these is influenced by the acidity of the solution.

2. *Variation of Manganous Sulphate.*—At the ordinary temperature in a dilute and feebly acid solution, permanganic acid acts very slowly upon oxalic acid, but the presence of a manganous salt, formed by its reduction or previously added, causes a great acceleration. This acceleration is shown to reach a maximum when three molecules of manganous sulphate are taken to one of permanganate. By the reaction of these quantities man-

ganic binoxide is formed according to the equation



3. *Variation of Oxalic Acid.*—The results obtained in this series of experiments are at first sight paradoxical. The quantity of permanganate reduced in three minutes, which was the time allowed to each experiment, increases with the proportion of oxalic acid up to a certain point; it then diminishes until another point is reached, after which further additions of oxalic acid produce again a very gradual acceleration. The result is the same whether only oxalic acid, potassic permanganate and manganous sulphate are taken, or whether sulphuric acid is added to these. The maximum action occurs with five molecules of oxalic acid and one of permanganate, that is with proportional quantities. The second and constant minimum is nearly attained with ten molecules of oxalic acid. Probably the manganic binoxide formed by the reaction of manganous sulphate and potassic permanganate combines with an excess of oxalic acid to form a compound whose decomposition proceeds more slowly than the action of free binoxide upon it. The conditions of the minimum action may be thus represented:—



There is found in the first instance a clear brown solution, the colour of which slowly fades.

4. *Variation of the Time.*—If it were possible for all other conditions of a chemical change to remain constant, if, for example, the substances reacting could be added in proportion as they disappeared, and those formed either were without influence or could be removed, the effect of a variation of time might be confidently predicted. In such a case the total amount of chemical change would be directly proportional to the duration of the action. But when one or more of the substances diminishes in quantity as the change proceeds, the relation is no longer of this simple character. Experiments upon this relation form the remaining and chief part of this inquiry. Each experiment of a series exactly resembled every other except in the time allowed to elapse before the action was interrupted. And thus each series may be regarded as exhibiting the course of a single experiment, and showing how much of the active substances still remain at any time from its commencement.

In the earlier series the reagents were employed in proportional quantities, and it was observed that for most of the determinations the product of the number expressing the duration of the action and of the number expressing the amount of active substance still remaining, is a constant quantity. The first stages of the action exhibit, however, a divergence from this law. This divergence is explained by reference to the simultaneous occurrence of two gradual actions, that in which manganic binoxide is formed and that in which it is reduced. The inverse proportionality of the residue to the duration of the action when two substances present in

proportional quantities are destroying one another, is shown to follow from a law the generality of which the authors hope to establish—namely, that the total amount of chemical change varies directly with the amount of each of the substances partaking in it.

In the later series of experiments the necessary condition, that the ratio of the reagents should remain constant throughout the action, was fulfilled by taking all but one of them in great excess as compared with that one. Under these circumstances a single substance gradually disappears, all around it remaining unchanged; and according to the law above enunciated, the total amount of change occurring at any moment is proportional to the quantity of substance then remaining. It is shown that if this be the case, the numbers representing the amounts of residue after equal intervals of time should form a series in geometric progression. This relation is actually exhibited by some of the experimental series; but the greater number of them do not conform to it. The reason of this is to be found in the fact that more than one reaction occurs under the circumstances of these experiments, and that it is only possible to measure the total effect. Experiments upon the solution in which the gradual oxidation of oxalic acid has taken place are adduced to show that some other oxidized product besides carbonic acid is formed, and it is inferred that more than one agent takes part in its oxidation. Also the facility with which hydrated peroxide of manganese reacts with dilute sulphuric acid and manganous sulphate to form a solution of mangano-manganic sulphate renders it probable that this salt is produced in the experiment. With an excess of oxalic acid and manganous sulphate the red colour of potassic permanganate disappears as soon as this salt is added to the mixture. The formation of manganic bin-oxide appears to be instantaneous. It finds itself in presence of two substances, both of which act gradually upon it—oxalic acid and manganous sulphate, the latter producing an intermediate oxide, probably the protoses-qui-oxide, which is also reducible by oxalic acid. It is possible that other oxides besides these may be formed; but it is almost certain, from the experimental results, that the action is not more simple than this. At the end of each experiment both or all of these oxides are alike instantaneously reduced by hydriodic acid and thus measured conjointly. Finally it is shown that an equation may be constructed embodying this hypothesis, and that all the series of experimental numbers may be expressed by equations of this form. The paper concludes with a mathematical discussion, by Mr. Esson, of various points in the theory of this action. An outline of his statement is here appended.

When a single substance is undergoing chemical transformation under constant conditions, it is shown by experiment that the law of connexion between y , the quantity of substance remaining unchanged, and x , the time during which the change has been proceeding, is $y = a\alpha^x$; where a is the quantity of substance present at the beginning of the change, and α a con-

stant which depends upon the conditions under which the change takes place. From this equation is derived $dy \propto y dx$, which expresses the fact that the amount of change varies directly with the time and with the quantity of substance.

Cases of complex chemical change can be investigated by the application of this general law. When two substances are reacting in proportional quantities, the amount of change is proportional to the amount of each, and the equation for determining the character of the reaction is $dy \propto y^2 dx$, or $\frac{1}{y} - \frac{1}{a} = \frac{x}{b}$, where a is the quantity of substance present at the beginning of the change. If a is very large, the equation reduces to $xy = b$, i. e. the quantity of substance remaining unchanged varies inversely as the time.

It is shown that the complexity of the results obtained in the experiments on the decomposition of potassic permanganate is probably due to the fact that there are two substances undergoing change, and that one of these substances is gradually formed from the other. The equations for determining the character of this reaction are

$$\left. \begin{aligned} \left(\frac{du}{dx} \right) &= -(\alpha + \beta)u, \\ \left(\frac{dv}{dx} \right) &= \beta u - \gamma v. \end{aligned} \right\}$$

From these equations are derived

$$u = ae^{-(\alpha + \beta)x}, \quad \dots \dots \dots (1)$$

$$v = \frac{\alpha\beta}{\alpha + \beta - \gamma} \left\{ e^{-\gamma x} - e^{-(\alpha + \beta)x} \right\}, \quad \dots \dots \dots (2)$$

$$y = \frac{a}{\alpha + \beta - \gamma} \left\{ \beta e^{-\gamma x} - (\alpha - \gamma) e^{-(\alpha + \beta)x} \right\}, \quad \dots \dots \dots (3)$$

where u is the quantity of one substance decomposed at the rate α , v the quantity of the other substance formed from u at the rate β and decomposed at the rate γ , y the whole quantity of substance capable of change, a the quantity of substance present at the beginning of the change, and x the time during which the change has been proceeding. Equation (3) admits of the forms

$$y = a_1 \alpha_1^x - b_1 \beta_1^x,$$

$$y = a_1 \alpha_1^x,$$

$$y = a_1 \alpha_1^x + b_1 \beta_1^x,$$

according as α is $> = < \gamma$. By varying continuously one of the conditions of the reaction, it is possible to obtain in succession values of α and γ , such that α is first $> \gamma$, and then $= \gamma$, and finally $< \gamma$; and thus these three forms of curves may occur in an investigation on the effect of varying one of the conditions of a reaction of this kind.